

Initiation of Lipid Peroxidation by Iron Complexes

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Lipid peroxidation can be initiated directly by several chelates of ferrous iron. A lag period is observed and its duration is longer for ferrous chelates which autoxidize slowly or under conditions which slow their rate of autoxidation. The lag period can be eliminated by an equal molar amount of the ferric chelate. Initiation by the ferrous chelates is unaffected by catalase unless the formation of the necessary ferric chelate involves oxidation by hydrogen peroxide. Also, hydroxyl radical scavengers have no effect on these systems. These results suggest that initiation may occur by some type of chelate-ferrous-oxygen-ferric-chelate complex. Thus, any reductant which can reduce the appropriate iron chelate may initiate lipid peroxidation. We have shown these to include superoxide, NADPH-cytochrome P450 reductase, glutathione, or cysteine. The control of cellular lipid peroxidation must therefore involve control of the redox state or reactivity of iron.

Is  $\alpha$ -Tocopherol Really the Best Chain-Breaking Antioxidant?

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Some  $\alpha$ -tocopherol analogues have been tested to determine the effects of variation of ring size, ring heteroatom and side chain upon the rate constant for the reaction of antioxidant with peroxy radicals. Only one compound has been found, so far, that is significantly more reactive than  $\alpha$ -tocopherol.